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[54] Pressurized gas packing and propellants for aerosols

[57] The invention relates to a pressurized gas packing, in particular an aerosol pressurized gas packing containing pressure-liquefied 2-hydroheptafluoropropane (F 227) or a mixture thereof with pressure-liquefied propane and/or *n*-butane and/or *i*-butane and/or dimethyl ether and/or 1,1-difluoroethane. Furthermore, the invention relates to a propellant for aerosols consisting of F 227 or its stated mixtures.

Pressurized gas packing and Propellants for Aerosols

For decades, aerosol pressurized gas packing, called aerosols for short, have been produced with the use of pressure-liquefied gases (in some cases, compressed gases as well) as propellant and used for various purposes. Used as pressure-liquefied gases (hereinafter also called "liquefied gases") are essentially the combustible gases propane/butane (P/B) and dimethyl ether (DME), as well as the noncombustible chlorofluorocarbons (CFCs), especially types 12 (dichlorodifluoromethane) and 114 (dichlorotetrafluoroethane).

The combustible liquefied gases involve some measure of safety risk. For this reason, the noncombustible and toxicologically safe CFCs have been preferably used. The likewise noncombustible compressed gases, such as CO_2 or N_2, can be used in only special cases because in pressurized packing they cannot maintain the constant pressure independent of the degree of discharge.

Since the establishment of the ozone theory (degradation of the ozone by CFCs and other organic compounds containing chlorine), there has been a search for liquefied gases suitable as propellants that are neither combustible nor able to degrade ozone and, moreover, are not harmful to health.

A great variety of pressurized gas packings in terms of their technical application properties can be produced with the use of pressure-liquefied gases. Pressurized gas packings always consist of a pressure container, preferably made of metal or glass, that is equipped with a valve mechanism for the withdrawal of the contents of the packing, and of the packing material in the container. The packing material can be of diverse nature.

In the simplest case, it consists only of a single pressure-liquefied gas, which is released into the air from containers without standpipes when the valve is actuated from the gaseous phase, i.e., in the gaseous state, thereby producing a compressed-air-like (puffing) effect. Such products are used for removing dust from, e.g., glass surfaces such as camera lenses.

In the great majority of cases, the contents of the container consist of what is called a packing material (often also called solution of active substance) that is to be sprayed and a propellant in the form of pressure-liquefied gas or gaseous mixture, which is miscible in the liquid phase with a liquid packing material in any proportion, thus forming only a single liquid phase over which a gaseous phase forms. Examples of such (true) aerosol products, which are sprayed from the packing as a mist, are, e.g., insecticide sprays, room sprays, deodorant sprays. These have a relatively high proportion of propellant (> 50%). A requirement for its functioning capacity is uninterrupted miscibility of the packing product solvent with the liquefied propellant (mixture) as well as the use of a valve with a standpipe that reaches to the bottom of the container.

Another type of aerosol product are the foam aerosols, in which the liquid portions of the packing product (e.g., water) do not form a homogeneous liquid phase with the pressure-liquefied propellant gas because of the lack of miscibility, but form two separate liquid phases. When the container is shaken in the presence of a surface-active agent, the two liquid phases form an emulsion (usually an O/W, or "oil-in-water" emulsion). Upon emerging from the container through the valve with a "foaming head," the emulsion changes to a foam because of the sudden vaporization of the oil phase (i.e., the liquid gas droplets), the volume of which is 200 to 300 times greater than that of the emulsion. Such foam aerosols are mainly used in the cosmetic field (e.g., for shampoos, shower foam, sunscreen foam). A prerequisite for their production is that the packing product and liquid gas do not mix homogeneously, which signifies a very low solubility of the liquefied gas phase in the liquid packing product phase; this is generally a given when the packing product is in aqueous form, namely, "water-based."

Known from DE-OS 1,542,076 are propellant mixtures that contain a relatively water-soluble propellant from the group of liquefied halogenated hydrocarbons and a relatively water-insoluble propellant of the same group. In this connection, 2H-heptafluoropropane is cited as an example of a relatively water-insoluble propellant.

A subject of the invention is a propellant for aerosols consisting of pressure-liquefied 2-hydroheptafluoropropane (F 227) or the mixture thereof with pressure-liquefied propane and/or *n*-butane and/or *i*-butane and/or dimethyl ether and/or 1,1-difluoroethane. The propellant is preferably a mixture of F 227 with propane and/or *n*-butane and/or *i*-butane and/or dimethyl ether.

But F 227 can also be used for blowing away dust, from, e.g., glass surfaces such as camera lenses. In that case, a suitable pressurized gas packing contains only pressure-liquefied F 227. Contrary to this, an aerosol pressurized gas packing contains, in addition to F 227 or its stated mixture (as propellant), a packing material in which the propellant and packing material can form a single or also two liquid phases.

An especially important case are aerosol pressurized gas packings in which the packing material contains water as the liquid portion; in that case, the packing material is generally an aqueous solution, but sometimes also a suspension. In that case, a second liquid (i.e., aqueous) phase is always present in addition to the pressure-liquefied propellant (F 227 or its stated mixtures).

The pressure-liquefied mixture components propane, *n*-butane, *i*-butane, dimethyl ether and 1,1-difluoroethane all have a density of less than 1 g/cm^3, whereas F 227 has a density of more than 1 g/cm^3. Therefore, mixtures with a density of about 1 g/cm^3 can be prepared from F 227 and the stated mixture components. Such mixtures thus have the same or a very similar density as an aqueous phase and are consequently very suitable as propellants for water-based aerosols. In appropriate pressurized gas packings, even the first shaking produces stable O/W emulsions that

no longer separate in two continuous phases even upon prolonged standing and hence need not be shaken again before being reused.

The following propellant mixtures are especially well suited for water-based aerosols:

1. A mixture of F 227 and propane/*n*-butane (mass ratio of 15 : 85) in a mass ratio of 65 : 35 to 85 : 15, preferably of 70 : 30 to 80 : 20, especially of about 75 : 25.

2. A mixture of F 227 and *i*-butane in a mass ratio of 65 : 35 to 85 : 15, preferably 70 : 30 to 80 : 20, especially about 74 : 26.

3. A mixture of F 227 and propane/*i*-butane (mass ratio 65 : 35) in a mass ratio of 70 : 30 to 90 : 10, preferably 75 : 25 to 85 : 15, especially about 80 : 20.

4. A mixture of F 227 and 1,1-difluoroethane (F 152 a) in a mass ratio of 35 : 65 to 45 : 55, especially about 40 : 60.

One of the propellant mixtures 1 through 3 is preferably used.

Examples

The followed propellant mixtures I through V were prepared:

Components	I	II	III	IV	V
	(% by weight)	(% by weight)	(% by weight)	(% by weight)	(% by weight)
F-227	76.0	65.0	40.0	74.0	80.0
Propane	3.6	-	-	-	13.0
n-Butane	20.4	-	-	-	-
i-Butane	-	-	-	26.0	7.0
F 152 a	-	-	60.0	-	-
DME	-	35.0	-	-	-
Total	100.0	100.0	100.0	100.0	100.0
Density (kg/L)					
20° C	1.0	1.0	1.06	1.0	1.05
50° C	0.9	0.9	0.97	0.9	0.96
Pressure (bar)					
20° C	3.6	4.7	5.3	3.5	5.3
50° C	8.2	10.7	11.4	8.0	11.5

Example 1 (shaving cream)

The following aerosol fillings were prepared in aerosol glass bottles with a commercial aerosol valve and foam head:

Filling product:

9.0 percent by weight of stearic acid

1.0 percent by weight of polyglycol 400

1.0 percent by weight of polyglycol 1500
2.0 percent by weight of lauric acid monoethanolamide
3.0 percent by weight of glycerol
4.0 percent by weight of industrial triethanolamine
80.0 percent by weight of distilled water.

The filling product was filled with propellant mixtures I, III, IV or V in a ratio of
90 percent by weight of filling product
10 percent by weight of propellant mixture.

In all 4 cases, an emulsion was obtained after shaking that was stable in storage and no longer separated into 2 continuous liquid phases, even after months of standing. On depressing the foam head, a finely porous, stable foam whose properties met all the requirements of a shaving cream was obtained in every case. All the foams, even those with the propellant mixtures I, IV and V, could not be ignited, unlike the commercial shaving cream aerosols filled with propane/butane.

Example 2 (shower foam)

As in Example 1, test fillings of aerosol shower foams were prepared according to the following formulation:
Filling product:
3.0 percent by weight of isopropyl myristate
2.0 percent by weight of 1,2-propylene glycol
60.0 percent by weight of sodium alkylpolyglycol ether sulfate
10.0 percent by weight of palm kernel fatty acid sarcoside
25.0 percent by weight of distilled water.
Filling ratio:
90 percent by weight of filling product
10 percent by weight of propellant mixture.

As in Example 1, the mixtures I, III, IV and V were introduced as the propellant phase.

The results obtained were analogous to those of Example 1. These foams also proved to be non-flammable.

Example 3 (body deodorant spray)

The following test filling was prepared in aerosol glass bottles:

Filling product	

96.1 percent by weight	Ethanol (99.8%)
0.5 "	5-Chloro-2-(2,4-dichlorophenoxy)phenol
1.0 "	Isopropyl myristate
0.4 "	Perfume oil
2.0 "	1,2-propylene glycol
100.0 "	

Filling ratio:
30.0 percent by weight of filling product
70.0 percent by weight of propellant

As propellant, we used pure F 227 once and propellant mixture II once. Both filling products had excellent spray characteristics and were stable in storage at –5°C as well as at +40°C. In terms of odor, the filling with mixture II still surpassed the perfectly flawless filling with pure 2-hydroheptafluoropropane. According to EU legislation, fillings with pure F 227 as propellant do not have to be labeled as "FLAMMABLE".

Example 4 (perfume spray)

A perfume spray of the following composition was prepared:

Filling product:	
5.0 percent by weight	Perfume oil
95.0 "	Ethanol (96%)
100.0 "	

Aerosol filling:
40.0 percent by weight of filling product
60.0 percent by weight of propellant F 227

The test sample exhibited excellent spray properties and stability in storage. There was no impairment of the fragrance due to the propellant. According to EU guidelines, products prepared according to this formulation do not have to be labeled as "FLAMMABLE".

Claims

1. Propellant for aerosols consisting of pressure-liquefied 2-hydroheptafluoropropane or mixtures thereof with pressure-liquefied propane and/or *n*-butane and/or *i*-butane and/or dimethyl ether and/or 1,1-difluoroethane.

2. Use of pressure-liquefied 2-hydroheptafluoropropane or its mixture with pressure-liquefied propane and/or *n*-butane and/or and/or *i*-butane and/or dimethyl ether and/or 1,1-difluoroethane as propellants for aerosols.

3. Use of pressure-liquefied 2-hydroheptafluoropropane for blowing away dust.

4. Pressurized gas packing containing pressure-liquefied 2-hydroheptafluoropropane or mixture thereof with pressure-liquefied propane and/or *n*-butane and/or *i*-butane and/or dimethyl ether and/or 1,1-difluoroethane.

5. Aerosol pressurized gas packing containing a propellant and a filling product, that can form one or two liquid phases, with the propellant consisting of pressure-liquefied 2-hydroheptafluoropropane or mixture thereof with pressure-liquefied propane and/or *n*-butane and/or *i*-butane and/or dimethyl ether and/or 1,1-difluoroethane.

6. Aerosol pressurized gas packing according to claim 5, characterized in that the filling product contains water as the liquid portion and forms a second liquid phase.

7. Aerosol pressurized gas packing according to claim 6, characterized in that a mixture consisting of pressure-liquefied 2-hydroheptafluoropropane and propane and/or *n*-butane and/or *i*-butane and/or dimethyl ether and/or 1,1-difluoroethane that has approximately the same density as the filling product containing water is used as propellant.

8. Aerosol pressurized gas packing according to claim 6, characterized in that a mixture of 2-hydroheptafluoropropane and propane-butane (mass ratio 15 : 85) is used as propellant in a weight ratio of 65 : 35 to 85 : 15.

9. Aerosol pressurized gas packing according to claim 8, characterized in that the mass ratio is 70 : 30 to 80 : 20.

10. Aerosol pressurized gas packing according to claim 6, characterized in that a mixture consisting of 2-hydroheptafluoropropane and *i*-butane is used as propellant in a mass ratio of 65 : 35 to 85 : 15.

11. Aerosol pressurized gas packing according to claim 10, characterized in that the mass ratio is 70 : 30 to 80 : 20.

12. Aerosol pressurized gas packing according to claim 6, characterized in that a mixture of 2-hydroheptafluoropropane and propane/*i*-butane (mass ratio 65 : 35) is used as propellant in a mass ratio of 70 : 30 to 90 : 10.

13. Aerosol pressurized gas packing according to claim 12, characterized in that the mass ratio is 75 : 25 to 85 : 15.

14. Aerosol pressurized gas packing according to claim 6, characterized in that a mixture of 2-hydroheptafluoropropane and 1,1-difluoroethane is used as propellant in a mass ratio of 30 : 70 to 50 : 50.

15. Aerosol pressurized gas packing according to claim 15*, characterized in that the mass ratio is 35 : 65 to 45 : 55.

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* Sic.—*The Language Service.*

Patent claims for the following Convention countries: ES, GR

1. Process for spraying aerosols, characterized in that pressure-liquefied 2-hydroheptafluoropropane or mixture thereof is used with pressure-liquefied propane and/or *n*-butane and/or *i*-butane and/or dimethyl ether and/or 1,1-difluoroethane as propellant.

2. Process for blowing away dust, characterized in that pressure-liquefied 2-hydroheptafluoro- propane is used for the blowing.

3. Process for spraying aerosols by means of an aerosol pressurized gas packing containing a propellant and a filling product that can form one or two liquid phases, characterized in that the propellant consists of pressure-liquefied 2-hydroheptafluoropropane or mixture thereof with pressure-liquefied propane and/or *n*-butane and/or dimethyl ether and/or 1,1-difluoroethane.

4 Process according to claim 3, characterized in that the filling product contains water as the liquid portion and forms a second liquid phase.

5. Process according to claim 4, characterized in that a mixture consisting of pressure-liquefied 2-hydroheptafluoropropane and propane and/or *n*-butane and/or *i*-butane and/or dimethyl ether and/or 1,1-difluoroethane that has approximately the same density as the filling product containing water is used as propellant.

6. Process according to claim 4, characterized in that a mixture consisting of 2-hydroheptafluoropropane and propane/*n*-butane (mass ratio 15 : 85) is used as propellant in a mass ratio of 65 : 35 to 85 : 15.

7. Process according to claim 6, characterized in that the mass ratio is 70 : 30 to 80 : 20.

8. Process according to claim 4, characterized in that a mixture consisting of 2-hydroheptafluoropropane and *i*-butane is used as propellant in a mass ratio of 65 : 35 to 85 : 15.

9. Process according to claim 8, characterized in that the mass ratio is 70 : 30 to 80 : 20.

10. Process according to claim 4, characterized in that a mixture consisting of 2-hydroheptafluoropropane and propane/*i*-butane (mass ratio 65 : 35) is used as propellant in a mass ratio of 70 : 30 to 90 : 10.

11. Process according to claim 10, characterized in that the mass ratio is 75 : 25 to 85 : 15.

12. Process according to claim 4, characterized in that a mixture consisting of 2-hydroheptafluoropropane and 1,1-difluoroethane is used as propellant in a mass ratio of 30 : 70 to 50 : 50.

13. Process according to claim 12, characterized in that the mass ratio is 35 : 65 to 45 : 55.